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ORIGINAL ARTICLE

Elemental analysis of steel products using X-ray fluorescence (XRF) technique

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Abstract The objective of this research project was to determine the elemental composition of steel products manufactured by the most popular company in the country. The analysis by independent institution will be instructive for the consumers and helpful for the manufacturer company in order to upgrade the quality of its final steel products. The X-ray fluorescence (XRF) technique was used in this work to determine the elemental composition of long and flat steel products manufactured by this local company. The long products analyzed in this research work are some concrete reinforcing bars and wire rods, while the flat products analyzed including hot and cold rolled coils, and zinc galvanized coils. The results of these analyses show that most elemental compositions obtained conform to the values claimed by the company except that for silicon and manganese which exhibit slightly higher value for some long products. Nevertheless, the elemental compositions obtained for flat products conform to the specifications claimed by the company.

1. Introduction

The fast growth in the Gulf region and especially in the Kingdom of Saudi Arabia in the last few decades was accompanied by large building construction and industrial activities. The quantities of steel products needed for different construction and industrial activities are enormous. Most of the steel products used for this purpose are the reinforcing bars, wire rods, rolled coil and galvanized coil sheet plate. The determination of chemical compositions of these products is very important not only for the users but also for the manufacturer as well.

The steel products manufactured by this local company and purchased for this study are composed of some long products and some flat products. The selected long products are concrete reinforcing bars and wire rods which are used

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extensively in building constructions and in various infrastructures. The selected flat products are rolled coil and galvanized coil sheet plate which are used for many purposes such as air-conditioning, panels and appliance industries. The different samples, manufactured by the company, were randomly collected from the Saudi market.

The elemental composition of the steel products was performed by the X-ray fluorescence technique (XRF). The XRF technique has many advantages; it is fast, accurate, non destructive and has a limit of detection in the range of few part per million (ppm) of most elements (Al-Eshaikh and Kadachi, 2006; Ida et al., 2005). For these reasons, the XRF analysis method is widely used in many fields such as metallurgy, industry, geology and mineralogy, food industry and environmental management. The analysis of steel is useful for various purposes, such as the inspection of raw materials, intermediate product and end products, process control in iron, steel manufacturing and quality control (Hou et al., 2004). However, most of routine steel analysis involve standard wet chemical method or inductively coupled plasma atomic emission. These methods are destructive and require dissolution of the alloy and long sample preparation (Nham, 1991). Use of X-ray fluorescence technique is very attractive in many fields and especially for metal and alloy analysis (Goldsttein and Sivilis, 2002; Rutherford, 1993). The sample preparation for XRF is relatively simple that require less time consumption and effort. For example, when the solid sample is homogeneous then it needs only polishing to be ready for analysis (Blank and Eksperiandova, 1997).

Many steel manufacturers in the world including those of the Gulf region make their steel products according to different national or international standards such as ASTM, BS, and JIS, etc. (ASTM, ISO, BS, JIS). The results obtained in this work will be compared with the values given in the different grade standards or with the claimed values given by the manufacturing company for the verification of conformity. The chemical compositions of steel products, determined by independent institution, are very important not only for the users but also for the manufacturer who can use the result to improve the quality of its products.

2. Materials and methods

2.1. Materials

In this project, some long products such as concrete reinforcing bars and wire rods were analyzed using XRF technique to determine their elemental compositions. Some flat products such as rolled and galvanized coil were also analyzed. These products are used in building constructions and in many industrial fields to manufacture different goods and appliances. The samples of each above steel products were collected from the local Saudi Arabia market. The sample preparation is an important step that can affect the precision and the accuracy of the XRF analysis. Therefore, two conditions at least must be satisfied, the first one is that the sample must be representative of the entire material and the second is that the surface of the sample must be smooth to reduce the diffraction of the X-ray (Grieken and Markowicz, 2002).

2.2. Equipments

The energy dispersive X-ray fluorescence spectrometer (EDXRF) unit, JSX-3202-M used in this project was manufactured by JEOL Company in Japan. This unit is able to analyze a wide range of specimen samples in the form of solid, powder and liquid. The elements, that can be measured by this instrument unit range from sodium (Na) to uranium (U). The spectrometer consists of the main unit and a computer system. The main unit incorporates an X-ray tube, an Si(Li) detector with 133 eV resolution at 5.9 keV (Mn Kα), an analyzing chamber and a specimen chamber. The computer system contains the software to drive the unit and spectrum analysis software. This software allows simultaneous multi-element spectral measurement, and qualitative and quantitative elemental analysis using fundamental parameter (FP) and reference methods. The detection limit of the system varies from 10 to 100 ppm depending on the inverse of the atomic weight of the element.

3. Methods

The *qualitative analysis* is the identification of all elements present in the X-ray fluorescence spectra, which is based on the determination of the correct top position of each peak (centroid). The conversion of the peak centroid channels to energies lines is made using energy calibration curve. Therefore, different standard references elements with known energies lines K_α or K_β were chosen to cover the interesting energy region of 1–25 keV for this energy calibration. The spectrum obtained of each standard references were analyzed by spectrum analysis software to determine the energy–channel relationship using least square fitting method (Jeol, 2005). The linear energy–channel relationship calculated is expressed as following:

$$E\ (\mathrm{keV}) = A + BX \tag{1}$$

where $A = 0.01000$; $B = 0.00216$ (keV/channels); X = number of channels.

This relationship is used to identify the unknown elements present in the spectrum with the help of X-ray lines energies database of all elements.

The *quantitative analysis* is the conversion of the net peak intensity present in the X-ray fluorescence spectra to element concentration. Therefore, the first step is to determine the correct net peak intensity of each X-ray line present in the analyzed sample. The spectrum analysis software was guided to deconvoluate the overlapping peaks and calculates the net peak intensity of each peak by subtracting the background using a mathematical model. The second step is to calculate the element concentration using a combination of the fundamental parameter (FP) method and the reference method. The FP is a method of theoretical calculation of the fluorescence X-ray intensity on the basis of the instrument's characteristics parameters and physical fundamental parameters including the photoelectric absorption coefficient, mass absorption and fluorescence yield rate. The reference method allows more accurate analysis providing some reference standards of known composition. This method has the advantage to combine the data collected from the measured spectra of the known references and the powerful FP method calculation to adjust the instrument parameters (Jeol, 2005; Al-Eshaikh and Kadachi, 2005).

4. Measurements

All steel products selected in this project were measured by XRF technique to determine their elemental compositions. The long products and the flat products were collected randomly from the local Saudi market. Three samples of 4 cm length were cut in the workshop from each long product types. Also, three samples from each flat product types were cut in square foil of about 16 cm^2. The second important treatment is grinding and polishing of the two faces of each sample. The last step of this sample preparation is the cleaning by acetone of the polished sample faces. Therefore, for each steel product there were six faces ready to be measured by XRF.

After the equipment setting, the XRF measuring time was fixed to 2 min that is enough to collect sufficient statistic counting even for the small peak present in the spectra (Montgomery and Runger, 1999). The spectrum of each sample was identified by a code containing the name of the manufacture, the number of the sample, the diameter and the number of the face. All spectra were stored in the hard disk of the computer and also in a flash memory for later analysis. As an example, Figs. 1 and 2 show the spectra obtained for long and flat products with their respective quantitative analysis.

5. Results and discussion

5.1. Verification of conformity

The verification of conformity is based on statistical hypothesis testing which needs in advance to fix the significance of level α

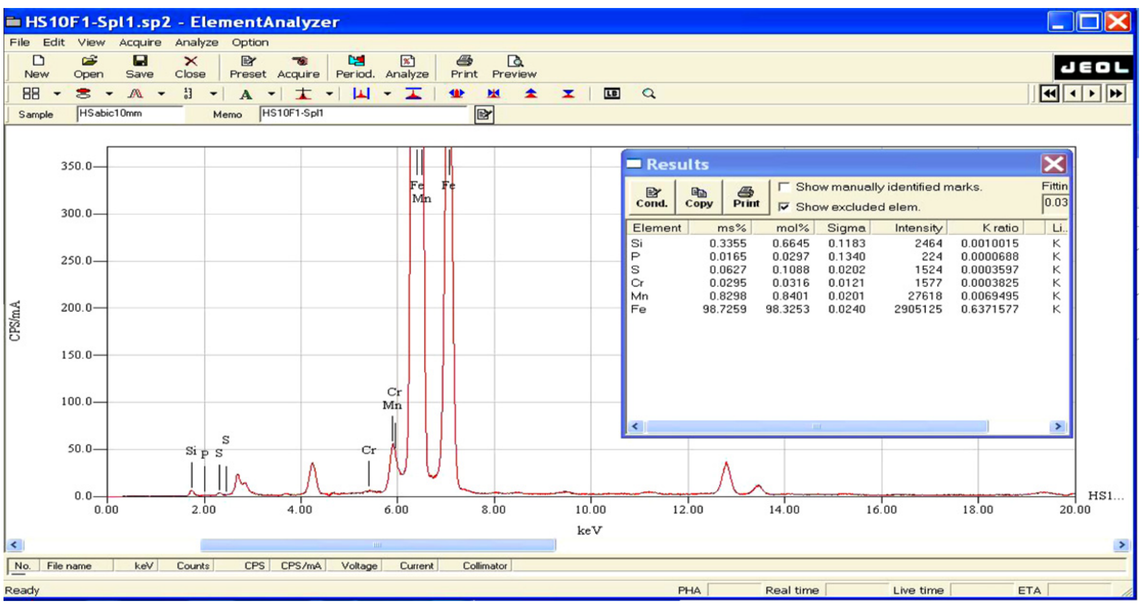

Figure 1 Spectrum of long product sample.

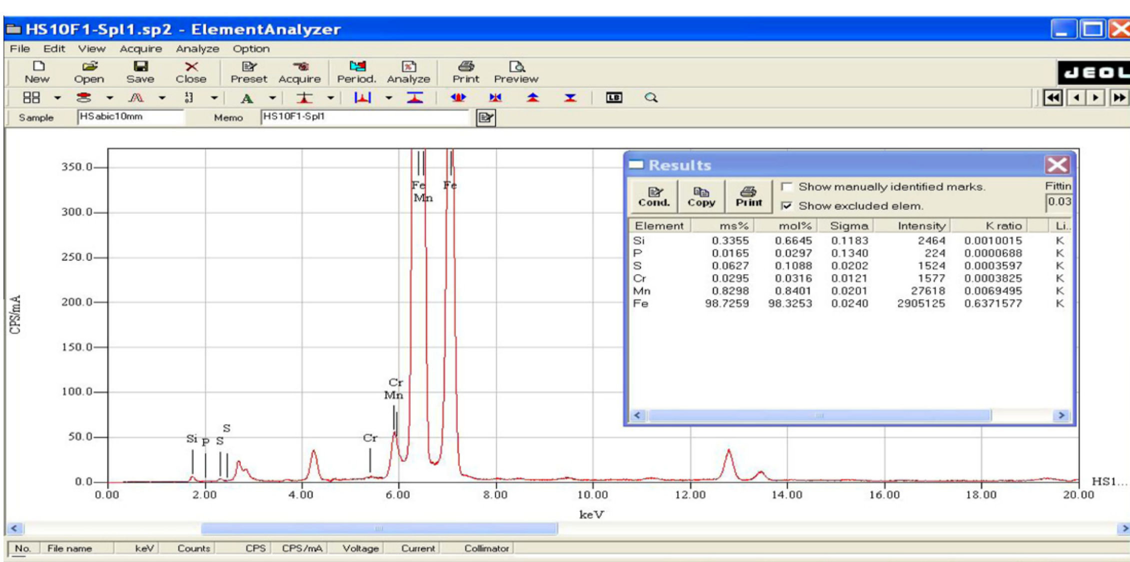

Figure 2 Spectrum of flat product sample.

and the value of the test statistic. In most engineering problems, the sample size is usually small and the confidence level must be at least equal to 95%. When the specification value (μ: the test value) must be less or more than a fixed value (μ_0 as a minimum or a maximum value), the test hypothesis is called one-sided hypothesis. In this case, the critical region is located at the left or at the right, with a fixed probability placed in the tail of the distribution (Montgomery and Runger, 1999). The test of hypothesis is then expressed by the null hypothesis, H_0 and the alternative hypothesis H_1 as following:

$$\begin{aligned} &H_0: \quad \mu = \mu_0 \\ &H_1: \quad \mu > \mu_0 \quad \text{or} \quad H_1: \quad \mu < \mu_0 \end{aligned} \tag{2}$$

The testing hypothesis methodology is based on the rejection of the null hypothesis and the acceptance of the alternative hypothesis, if the following conditions are fulfilled:

- For one-sided alternative hypothesis ($H_1: \mu > \mu_0$), minimum fixed value; the null hypothesis H_0 is rejected if:

  $$Y_0 = \frac{\overline{X} - \mu_0}{s/\sqrt{n}} > t[\alpha, n-1] \tag{3}$$

  where $\overline{X}$: the mean of the sample (average value); μ_0: the mean of the distribution; s: sample standard deviation; n: sample size; $t[\alpha, n-1]$: is a value extracted from Student distribution table.Another way to express this is to write the following formula:

  $$\mu = \overline{X} - t[\alpha, n-1] \cdot s/\sqrt{n} > \mu_0 \tag{4}$$

- For one-sided alternative hypothesis ($H_1: \mu < \mu_0$), maximum fixed value; the null hypothesis H_0 is rejected if:

  $$Y_0 < -t[\alpha, n-1] \tag{5}$$

  Another way to express this is to write the following formula:

  $$\mu = \overline{X} + t[\alpha, n-1] \cdot s/\sqrt{n} < \mu_0 \tag{6}$$

Note that, the p-value of the hypothesis test can be used also to reject the null hypothesis. The cutoff in these cases is 0.05, that is, reject the null hypothesis when the p-value is less than this value.

5.2. Long products

The chemical composition in % and the conformity of long products manufactured by this local company such as concrete reinforcing bars and wire rods are presented in the following tables.

According to statistical hypothesis testing mentioned above, the conformity is proved, if the test value μ is smaller than the manufacturer maximum claimed values (Hadeed Products). It can be noted from Tables 1 and 2 that most percentage values for the elements present are less than the maximum values except that of silicon and manganese for rebars and sulfur (S) for wire rods. Therefore, the company must put more effort to control the percentage level of these elements.

5.3. Flat products

The chemical composition in % and the conformity of flat products manufactured by this local company such as rolled coils and galvanized coils are presented in the following tables.

It can be observed in Tables 3–5 that the percentages of all elements present are less than the maximum value claimed by the manufacturer except that of sulfur in case of cold rolled

Table 1 Chemical composition conformity of rebars.

	Elements					
	C	Si	P	S	Cr	Mn
Claimed max. values	0.24	0.23	0.05	0.05	0.3	0.7
Average	–	0.5538	0.0169	0.0426	0.0249	0.8505
SE mean $= s/\sqrt{n}$	–	0.0444	0.0015	0.0040	0.0013	0.0117
p-Value	–	1.000	0.000	0.040	0.000	1.000
Test value μ	–	0.6310	0.0194	0.0495	0.0272	0.8708
Conformity	–	X	√	√	√	X

Table 2 Chemical composition conformity of wire rods.

	Elements			
	C	P	S	Mn
Claimed max. values	0.2	0.03	0.03	0.80
Average	–	0.0202	0.0737	0.5657
SE mean $= s/\sqrt{n}$	–	0.0024	0.0078	0.0024
p-Value		0.004	0.999	0.000
Test value μ	–	0.0250	0.0894	0.5705
Conformity	–	√	X	√

Table 3 Chemical composition conformity of hot rolled coils.

	Elements			
	C	P	S	Mn
Claimed max. values	0.2	0.035	0.035	1.60
Average	–	0.0185	0.0292	0.6614
SE mean $= s/\sqrt{n}$	–	0.0024	0.0014	0.0014
p-Value		0.000	0.004	0.000
Test value μ	–	0.0228	0.0317	0.6748
Conformity	–	√	√	√

Table 4 Chemical composition conformity of cold rolled coils (ASTM A611).

	Elements			
	C	P	S	Mn
Claimed max. values	0.27	0.035	0.035	0.90
Average	–	0.0144	0.0472	0.6399
SE mean $= s/\sqrt{n}$	–	0.0024	0.0031	0.0045
p-Value		0.000	0.999	0.000
Test value μ	–	0.0199	0.0527	0.6533
Conformity	–	√	X	√

Table 5 Chemical composition conformity of galvanized coils (ASTM-A653M).

	Elements			
	C	P	S	Mn
Claimed max. values	0.15	0.03	0.035	0.60
Average	–	0.0167	0.0256	0.0124
SE mean $= s/\sqrt{n}$	–	0.0023	0.0035	0.0017
p-Value		0.000	0.011	0.000
Test value μ	–	0.0209	0.0319	0.0155
Conformity	–	√	√	√

coils, which is little bit higher. Therefore, these steel flat products can be considered to conform to the claimed manufacturer specifications (ISO 10544 and other standards, www.iso.org).

6. Conclusions

The steel products manufactured by this local company and purchased for this study are composed of some long products and some flat products. The selected long products are concrete reinforcing bars and wire rods which are used extensively in building constructions and in various infrastructures. The selected flat products are rolled coil and galvanized coil sheet plate which are used for many purposes such as air-conditioning, panels and appliance industries. The different samples were randomly collected from the Saudi market. The analyses of these products, in this research project, are instructive not only for the consumers but also for the manufacturer company in order to upgrade the quality of its final steel products.

The energy dispersive X-ray fluorescence technique was used in this project to determine the chemical composition of the above steel products. The verification of conformity was done according to the values recommended in the specified standard or according to values claimed by the manufacturer.

The chemical composition conformity of long products manufactured by this local company such as concrete reinforcing bars and wire rods is proved for most elements except that of silicon and manganese for rebars and sulfur for wire rods. However, the company should put more effort in the control quality for the exceeding percentage elements (Si, S and Mn) or to rectify the maximum claimed values. The percentages of all elements present in flat products such as rolled coils and galvanized coils are less than the maximum value claimed by the manufacturer except that of sulfur in case of cold rolled coils, which exhibit little higher value. Therefore, these steel flat products can be considered to conform to the claimed manufacturer specifications.

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